

Interactive comment on “Mexico City aerosol analysis during MILAGRO using high resolution aerosol mass spectrometry at the urban supersite (T0) – Part 1: Fine particle composition and organic source apportionment” by A. C. Aiken et al.

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We thank Referee #3 for their support of the paper as a “comprehensive review . . . into the sources and evolution of the particulate air quality issue in Mexico City and other mega-cities in general and is highly recommended for publication in ACP.”

General Comments:

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(R3.1) Page 8384, line 21. The authors missed an opportunity to contribute to the understanding the role of collection efficiency (CE) in HR-ToF and other AMS data. Although CE was briefly mentioned and referenced, a detailed investigation into possible variations of CE and correlations with other measurements would have been extremely useful.

Response: The issue of CE has been addressed and discussed in detail in response to comment R1.1 from reviewer #1. We did perform additional detailed analyses that were not included in the paper because they did not produce an improvement over the composition-based estimate of CE=0.5. Indeed, this study was not really an “opportunity” to advance the knowledge on CE due to the lack of suitable measurements such as other speciated PM1 measurements (PILS, 1-hr Sunset OC) or true mass measurements (PM1 TEOM FDMS). We note that we summed the AMS concentrations with the BC, soil, and metal concentrations before comparing with the SMPS, so the comparison is also influenced by the accuracy and lower time-resolution of those measurements. The SMPS had a cut that was too low for comparison with the AMS, there were many non-spherical particles in the Mexico City environment which complicate the conversion of the SMPS data into apparent volume, and finally SMPS comparisons reveal accuracies often not better than 20%, as discussed above. The OPC-based PM1 instrument was scaled daily to true PM1 concentrations determined in filters and compares better with the AMS. We recognize an opportunity when we see one, but this was not the case in this study.

(R3.2) Page 8389 line 12-16. A quantification and perhaps a plot of the improvement in NH₄⁺ measurement noise would have been illuminating. Given the possible importance of organic nitrates, further discussion and quantification of their contribution would have been valuable.

Response: The main reason for the reduction of the noise in the NH₄⁺ measurement is the use of a ToF-AMS, as evidenced comparing Fig. 10 of Salcedo et al. (2006) with our Fig. S5. The improvement in noise due to using the HR ions is minor in this case,

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as evidenced by comparing Fig. S-5(a) with Fig. S-5(b) in the current manuscript. The relevant sentence has been changed to more accurately reflect this information:

"It also shows a clear reduction in the scatter due to the reduction in NH_4^+ measurement noise, mainly due to the use of a ToF-AMS, compared to Fig. 10 of Salcedo et al. (2006) which used the interference-subtracted UMR ions from a quadrupole-AMS. The reduction in noise due to the use of the directly-measured HR NH_x^+ ions instead of the estimation of the same ions with the fragmentation table (Allan et al., 2004) is minor in this case, although it may be more important at lower NH_4^+ concentrations."

Response: We have expanded the organic nitrate discussion to make clearer what our technique does and does not allow us to say at present:

"In terms of the organic nitrates (ONs), at present we are only able to state that their contribution to total nitrate and total OA is minor based on the ammonium balance. If the AMS nitrate signal was dominated by ONs there would be a large "ammonium deficit" and large scatter when the ammonium balance analysis is performed assuming that all of the AMS nitrate signal is ammonium nitrate. Neither effect is observed in Fig. S-5, which indicates that ammonium nitrate is the dominant form of nitrate in Mexico City, consistent with the aircraft measurements (DeCarlo et al., 2008), PILS measurements at T1 (Hennigan et al., 2008), and previous studies (Salcedo et al., 2006). This is also consistent with Gilardoni et al. (2009), who report the contribution of ONs and organosulfates to be small based on FTIR measurements on MILAGRO samples at several sites. In Mexico City ONs should make a similar fractional contribution to sub-micron OA (when the mass of all OA molecules that have a nitrate group is summed) than to submicron nitrate. For example, if 5% of the nitrate signal was due to ONs and we assume a MW of 250 amu for these species, the contribution of ONs to OA mass would be 4%. Additional laboratory calibrations in the HR-ToF-AMS with organonitrate standards are needed before a detailed assessment of their contribution to ambient OA can be performed. Our group and several other groups in the AMS community are active in that area (Farmer et al., 2008)."

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Minor Comments:

(R3.3) Page 8390, line 22. A more detailed discussion of the differences in non-refractory mass between aircraft and ground data would be helpful.

Response: We already discuss the differences in the nitrate fraction, while the fractions of the other species are similar. Note that the concentrations shown in Figure S-7 are from the whole campaign average (24 hrs) for T0, while the aircraft data is only from the average of only a few afternoon flyovers. Additionally, the comparison was also discussed previously in DeCarlo et al. (2008).

(R3.4) Page 8399 – sec 3.2.3. More explanation of the significance of OA/ ΔCO plots would help

Response: We have rewritten the text after the sentence introducing Fig. S-19 (now Fig. 11) as follows to address this point:

"The T0 data are bounded at the lower end by the low primary emissions ratio for urban HOA (Zhang et al., 2005c; Docherty et al., 2008; this study). The points near the HOA/ ΔCO lines are thus likely dominated by urban POA emissions. At the upper end the T0 data are bounded by values observed in both aged urban airmasses dominated by SOA (Volkamer et al., 2006; de Gouw et al., 2008; Kleinman et al., 2008; Dzepina et al., 2009) and forest fire emissions near Mexico City (Yokelson et al., 2007; DeCarlo et al., 2008). T0 is an urban setting and is heavily impacted by HOA emissions, but the dominant presence of higher OA/ ΔCO ratios indicates important impacts from SOA formation and/or biomass burning sources. However, since both SOA formation and forest fire emissions can produce the higher OA/ ΔCO ratios, their relative contributions cannot be separated with the OA/ ΔCO analysis alone. This contrasts with the use of the OA/ ΔCO technique in areas where only POA and SOA from urban pollution are thought to be making a major contribution, as under those circumstances the SOA contribution can be estimated with the "CO-tracer method" alone, which estimates POA as the measured ΔCO multiplied by the primary POA/ ΔCO ratio, and

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assigns the rest of the measured OA to SOA (Takegawa et al., 2006; Docherty et al., 2008). Similarly, the contribution of forest fires cannot be reliably estimated in our case with a similar method, since the urban OA/ Δ CO is not well-characterized and varies with photochemical age due to SOA formation."

Response: We have also added Fig S-19 to the main paper in response to comment R2.6 from referee #2.

(R3.5) Page 8402 line 4. The reference to possible differences in relative ionization efficiencies or CE's underscore the need for further analysis and discussion in these areas.

Response: We agree with this general need for the AMS community, but as discussed in response to comments R1.1 and R3.1 we believe that we had already extracted the information that was available in this study.

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